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► To cite this version:

A. Dauzères, A. Maillet, A. Gaudin, Abderrazak El Albani, Philippe Vieillard. Ten years of Toarcian argilite - carbon steel in situ interaction. *Procedia Earth and Planetary Science*, 2013, 7, pp.195-198. <10.1016/j.proeps.2013.03.056>. <hal-00918405>

HAL Id: hal-00918405

<https://hal.science/hal-00918405v1>

Submitted on 27 Sep 2021

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Water Rock Interaction [WRI 14]

Ten years of Toarcian argillite - carbon steel *in situ*
interaction

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Abstract

In situ interaction experiments over periods of 2, 6, and 10 years between Toarcian argillite and carbon steel discs were carried out in the Tournemire Underground Research Laboratory (URL), yielding a dataset of the materials' geochemical evolution under conditions representative of the future geological disposal of high-level long-lived radioactive wastes. The carbon steel discs were exposed to corrosion due to trapped oxygen. The corrosion rates indicate that the oxidizing transient lasted between 2 and 6 years. A systematic dissolution of calcium phases (Ca-smectite sheets in I/S and calcite) was observed in the iron diffusion halos. The iron release induced mineralogical dissolution and precipitation reactions, which partly clogged the argillite porosity.

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Selection and/or peer-review under responsibility of the Organizing and Scientific Committee of WRI 14 – 2013

Keywords : argillite; carbon steel; corrosion; oxidising transient; porosity, minerals.

1. Introduction

In the French concept developed by Andra for the high-level long-lived radioactive wastes disposal, wastes are emplaced in steel containers. These containers are inserted into disposal cells, which are mechanically supported using a carbon steel liner. Thus, a non-negligible amount of metallic materials lie in contact with the clayey environment [1]. Upon water fluxes coming from the host-rock, the iron will react with the surrounding argillite and will induce mineralogical transformations, causing containment

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properties changes in the host-rock. Reaction pathways related to the metal corrosion still remain to be further understood (evolution of pH, redox, and fluxes of soluble iron towards the argillite), and some other significant issues remain open: in particular the dissolution/precipitation processes in the argillite which are likely to alter its swelling properties and its cation exchange capacity (CEC), the prediction of the alteration plume (homogeneous alteration front) and the effects of these transformations on the materials containment performances.

As part of a project carried out in collaboration with EDF in the Underground Research Laboratory (URL) of Tournemire (Aveyron, France) [2], researches are conducted by IRSN to study the carbon steel/argillite interactions using data gathered from an *in situ* experiment in which carbon steel discs were placed in contact with a remoulded argillite for 2, 6, and 10 years. The present paper aims to i) illustrate reactive mechanisms in the carbon steel disc exposed to the aggressive clayey environment under the influence of the trapped oxygen after 10 years; ii) identify the physical-chemical evolution of the argillite exposed to the iron flux released by the steel corrosion.

2. Experimental and analytical approaches

The *in situ* test consisted to emplace five carbon steel discs within the argillite in the CR6 horizontal borehole (length: 10 m; diameter: 46 mm) drilled on the main tunnel West wall, see Fig. 1. Actually, the steel discs (A42 Carbon grade) were placed in the last meter of this borehole to be both out of the EDZ (Excavation Damaged Zone) and out of the unsaturated zone around the tunnel, and remoulded (crushed and compacted) argillite was placed between each carbon steel disc.

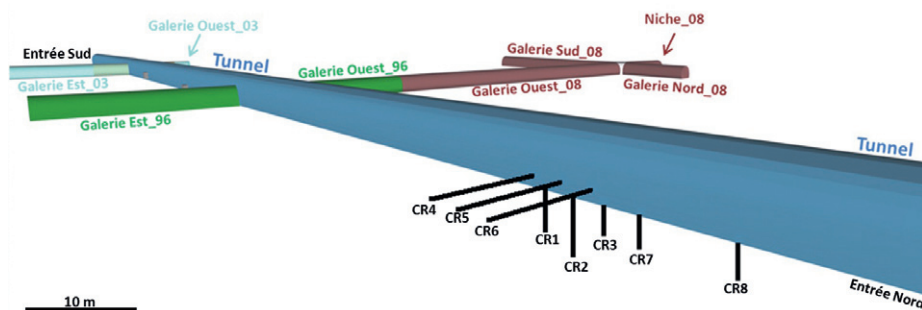


Fig. 1: Location of the CR6 borehole in the Tournemire URL.

The Tournemire argillite is dated from the Toarcian (180 million years). Its mineralogy (% weight) is composed of a dominant clayey fraction (60% in total: 16% illite, 30% I/S mixed-layer, 10% kaolinite and 4% chlorite), an important content of calcite and dolomite (15%), quartz (16%), K-feldspar (4%) and a small content of pyrite (2%) controlling the redox state of the natural rock. The argillite porosity reads 10% for the virgin rock and 45% for the remoulded material located between each steel disc. Porosity measurements were carried out by autoradiography after embedding with ^{14}C PMMA resin.

After 10 years of interaction, samples were extracted by over-coring (diameter 250 mm), and the last meter of the core was immediately placed in a sealing bag with a nitrogen atmosphere to prevent oxidation of possibly formed reductive phases. All the further preparation steps (cutting, embedding...) were carried out in a glove box under nitrogen atmosphere.

Several characterizations techniques were used to identify the physical-chemical evolution of the steel/argillite interface: XRD, μ -Raman spectroscopy, SEM-EDS, CEC, TGA-TDA for the chemical and mineralogical analyses; autoradiography, XR microtomography and BET for microstructure analyses.

3. Results and discussion

3.1. Mineralogical evolution

Inspection of steel/argillite composites evidences a heterogeneous corrosion of steel discs, with an alteration thickness ranging from 50 μm to 300 μm . This steel corrosion releases iron in the medium, which diffuses into the argillite, forming a halo. From observations carried out by XR microtomography (see Fig. 2), the maximal thickness of the iron perturbation within the argillite is estimated around 5 mm. Corrosion rates, estimated from the weight loss, show a decrease between 2 and 6 years (results were obtained with two other cores: CR4 and CR5), which suggests an oxidizing transient period longer than 2 years.

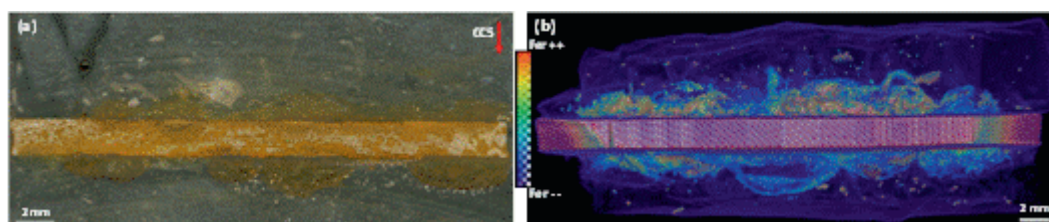


Fig. 2: Carbon steel/argillite interface. Iron diffusion into the argillite: (a) sample photography; (b) 3D XR microtomography section.

Macroscopically, the iron diffusion is recognizable by an orange color. The XRD, TGA and μ -Raman analyses highlight the iron oxides formation: goethite, hematite and magnetite. In parallel to the iron diffusion, all calcium phases (calcite and Ca-smectite sheets in I/S mixed layers) are dissolved, which is linked with the acidification of the argillite pore water solution. In a first approach, such an acidification was explained by the classical process of pyrite dissolution linked to a possible oxidation due to oxygen trapped in the argillite porosity. However, XRD analyses suggest a stability of the pyrite near the interface, in the volume affected by the Ca-phases dissolution.

Another hypothesis is proposed here, in consistency with the significant and systematic enrichment in sulphur recorded by SEM-EDS in the corrosion area of the steel disc. On the one hand, part of this enrichment is linked to the possible formation of sulphate green rust (morphological recognition by SEM), in agreement with geochemical modelling that suggests formation of this phase in such an environment. On the other hand, the sulphur concentration depends on the location in the corrosion area. In the corrosion area centre, the sulphur signal is diffuse, linked to the formation of green rust. Near the interface with argillite, the concentration in sulphur is more intense, linked with the possible presence of bacteria, Sulphate Reducing Bacteria (SRB). In this zone, the EDS imaging shows possible biological-like shapes. Previous studies have shown that the Tournemire rock has different types of bacteria : SRB, IRB (Iron Reductive Bacteria). This last has the ability, by its metabolism, to release H^+ in the system and to acidify the environment. BSR have the ability to metabolize sulphates in solution [3] and to fix it into the corrosion area.

3.2. Microstructural evolution

Autoradiography analyses highlight a strong porosity variation at the argillite/carbon steel interface. The steel corrosion zone is affected by a high porosity opening: equal to 2 or 3% in the steel disc, the porosity increases up to 30% in the goethite/sulphate green rust area. In the opposite, the high porosity in the sound zone of the remoulded argillite (45%) falls down to 20% near the interface with the steel (in the Ca-phase dissolution area). In other words, the iron perturbation induces a partial clogging of the clayey material porosity.

An additional interesting result is underlined by X-Ray microtomography analyses: strong cracks are observed in the argillite, due to the method used to prepare and install the remoulded argillite in the borehole. Analyses show that each iron diffusion halo and local corrosion gulf on the steel disc is linked with the occurrence of one or several cracks in the argillite. Natural water fluxes towards the borehole control the transport of aggressive ionic species, but this transport is enhanced by these cracks which then enhances the local corrosion of the carbon steel disc. The released iron seems to have also followed these paths, which induces the heterogenous diffusion.

4. Conclusion

This study of 10 years old *in situ* clay/carbon steel interactions in the Tournemire URL allows for highlighting potential physical-chemical processes relevant for future high level waste disposal cells:

- The carbon steel discs were exposed to the corrosion due to the trapped oxygen. The corrosion rates indicate that the oxidizing transient lasted between 2 and 6 years. Associated to classical corrosion processes, sulphur enrichment was consistently observed in the corrosion area, linked with the sulphate green rust formation and with the potential presence of SRB.
- In the argillite, a systematic dissolution of calcium phases (Ca-smectite sheets in I/S and calcite) was observed in the iron diffusion halos. This dissolution was interpreted as a result of bacteria activity and not pyrite dissolution, as the pyrite phase remains unaltered up to the interface with the steel.
- The carbon steel corrosion causes a porosity opening in the corrosion products (goethite/sulphate green rust) at interface. The iron release induces mineralogical dissolutions and precipitations, which partly clog the argillite porosity.
- The bacteria activity seems an important parameter in the geochemical evolution of the system. Further investigations must be conducted to better assess their effects on processes.
- The oxidizing transient is a key parameter controlling the system evolution. This phenomenon and its kinetics should better be considered and characterized to assess its impact on reactive pathways.

Acknowledgements

Authors wish to thanks EDF for its financial support and especially Dr. François Foct for his valuable help and advice.

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